

Raman Effect in Liquids and in Liquid Mixtures

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

1932

BY
ELIZABETH AYLOR CRIGLER

Raman Effect in Liquids and in Liquid Mixtures

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

1932

BY
ELIZABETH AYLOR CRIGLER

ACKNOWLEDGMENT

The author wishes to express her most sincere appreciation to Professor D. H. Andrews under whose direction this investigation was carried on. His valuable suggestions, constructive advice, and constant encouragement made possible the present work.

She takes pleasure in acknowledging her indebtedness to Professor J. C. W. Frazer whose interest, help, and advice during her course at The Johns Hopkins University have been invaluable.

She expresses her thanks for the helpful instruction received from Professors J. C. W. Frazer, W. A. Patrick, E. Emmet Reid, F. O. Rice, G. H. Cartledge, D. H. Andrews, H. C. Urey, and N. E. Gordon, and Doctors W. M. Thornton, Jr. and Emil Ott. She profited much from them as they broadened her field of knowledge and enabled her to develop a truer interpretation of facts.

The author also wishes to thank Professor R. W. Wood of the Department of Physics for his many valuable suggestions which facilitated her experimental work.



I. RAMAN SPECTRA OF DIPHENYLMETHANE, ALIPHATIC BROMIDES AND MERCAPTANS

Introduction

During the past five years experimental investigations and theoretical development of the Raman effect have contributed much to our knowledge of the structure and chemical behavior of molecules by identifying Raman lines with the chemical bond.¹ The energy changes represented by Raman lines were early associated with fundamental molecular frequencies,² and the relation of Raman frequencies to the vibrational energy of the molecule has recently been presented and discussed by Andrews.³

The present work includes a study of the Raman spectra of diphenylmethane, normal butyl and normal hexyl bromides, and normal amyl, normal hexyl, and normal heptyl mercaptans. It was suggested by the important function of Raman data in specific heat determinations and in the calculation of thermal energy associated with the vibrations of the different parts of the molecule.⁴

Apparatus

Light Source and Light Filter.—A helium spiral discharge tube similar to the one described by Wood,⁵ and made by the Claude Neon Company of Baltimore, furnished the light for exciting the Raman lines recorded for diphenylmethane. The copper gauze electrodes of this discharge tube were connected to an oil transformer which converted the 220 volts across the alternating circuit to approximately 20,000 volts. The helium line, λ 3888.6, was transmitted by a nickel oxide glass filter.

A Cooper-Hewitt quartz mercury arc, maintained between 35 and 45 volts, was used to excite the Raman lines of all other substances. An aluminum reflector concentrated the mercury light on the Raman tube. In some instances the 4046 mercury group was eliminated by a 0.5% acid quinine sulfate filter.

An iron arc, taking 4 or 5 amperes, furnished comparison spectra for measuring the Raman lines.

Raman Tube.—The Raman tube, similar to those used by Wood, was 2.5 cm. in

¹ Andrews, *Phys. Rev.*, **36**, 544 (1930); Bhagavantam, *Indian J. Physics*, **5**, 237 (1930); Kohlrausch, "Der Smekal-Raman Effekt," Julius Springer, Berlin.

² Raman, *Indian J. Physics*, **2**, 387 (1928); Raman and Krishnan, *Nature*, **122**, 278 (1928); Coblentz, *Phil. Mag.*, **7**, 203 (1929).

³ Andrews, *Ind. Eng. Chem.*, **23**, 1232 (1931).

⁴ Andrews and Southard, *Phys. Rev.*, **35**, 670 (1930); Smith and Andrews, *J. Am. Chem. Soc.*, **53**, 3644 (1931); Smith and Andrews, *ibid.*, **53**, 3661 (1931); McGraw, *ibid.*, **53**, 3683 (1931).

⁵ Wood, *Phil. Mag.*, **7**, 859 (1929).

diameter and had a capacity of 60–65 cc. Instead of grinding a plane face on the end of the tube after it was made, a thin piece of glass, plane on both sides, was fused to the end. To prevent stray light from fogging the spectra, the tapered end and all parts of the tube not directly illuminated by the arc were either painted black or wrapped with black tar tape.

Spectroscope.—A Hilger quartz spectroscope was used with the helium discharge tube. A Bausch and Lomb glass prism spectroscope was used to analyze the light from the mercury arc.

Comparator.—The Raman lines were measured with a traveling micrometer by comparison with known iron lines. These readings plotted against the international standard wave lengths for the iron lines enabled one to interpolate with fair accuracy the wave lengths of the Raman lines.

Materials.—Normal butyl and normal hexyl bromides were compounds which have been previously described by R. F. Deese.⁶ The mercaptans were pure compounds kindly loaned by Professor E. Emmet Reid and Doctor L. M. Ellis, Jr.⁷

Hammer Press Ultra Rapid plates, Agfa developer, and Eastman "hypo" were used in photographing the Raman spectra.

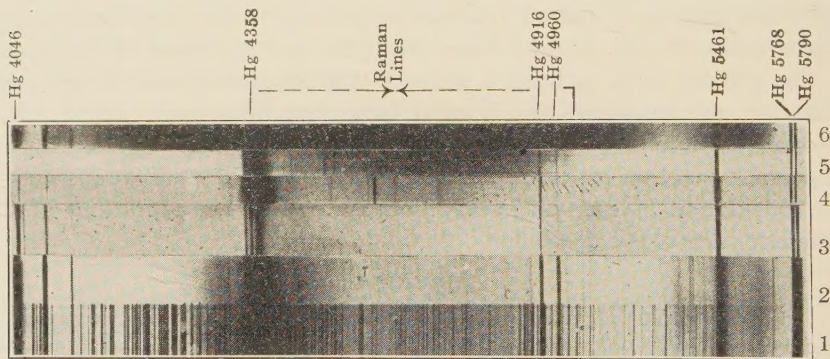


Plate I.—Comparison of spectra: 1, iron arc; 2, Hg arc (slit wide); 3, Hg arc (slit narrow); 4, benzene (quinine sulfate filter); 5, butyl bromide (quinine sulfate filter); 6, butyl bromide (no filter).

Technique and Procedure.—In general, Wood's method for obtaining Raman spectra was followed. In the set-up with the helium discharge tube, the Raman tube containing the diphenylmethane was slipped within the helium spiral, so that the substance under investigation was illuminated only by light passing through the nickel oxide glass filter. Forty-eight hour exposures were made. The photographic plates were backed with Duco enamel to prevent halation around the intense lines.

As the nickel oxide glass transmitted other helium lines, λ 3965 and λ 4045, falling in the same region as the Raman lines excited by the 3888.6 helium line, and since the Raman lines excited by the helium discharge tube were not as intense as those excited by the mercury arc, the latter was adopted as source of excitation for the remaining work.

In the set-up with the mercury arc the distance between the Raman tube and the spectroscope was 84 cm. The light coming from the face of the Raman tube was reflected by a small right angle prism down a long black iron tube to a double convex

⁶ Deese, *J. Am. Chem. Soc.*, **53**, 3673 (1931).

⁷ Ellis and Reid, *ibid.*, **54**, 1674 (1932).

lens which concentrated the light and focused a bright image of the prism face on the slit of the spectroscope. The prism was placed in a pasteboard box which fitted over the face of the Raman tube and the end of the iron tube in order to prevent reflection of stray mercury light.

Several preliminary experiments with the mercury arc showed the difficulties encountered in using the complete mercury spectrum. Most of the compounds investigated gave a continuous background in the presence of the 4046 mercury group. To eliminate this background the short-wave length mercury lines were absorbed by an acid quinine sulfate filter. The effect of this filter is shown in Plate I. The solution of quinine sulfate was slowly decomposed by the ultraviolet light from the quartz mercury arc, but by allowing it to circulate through a copper coil surrounded by a jacket containing ice and salt, the rate of decomposition was retarded sufficiently to allow time for an exposure of several hours.

Results

The third column in Table I gives the Raman lines for diphenylmethane. Photographs of these lines excited by the mercury arc were taken also; however, the lines were accompanied by such a dark continuous background that only results obtained with the helium discharge tube have been recorded. The diphenylmethane which was colorless

TABLE I
COMPARISON OF RAMAN LINES OF DIPHENYLMETHANE WITH THE RAMAN LINES OF
COMPOUNDS OF SIMILAR STRUCTURE

Values given in wave numbers $[\Delta\bar{\nu}] = \left[\frac{1}{\lambda_{\text{ex}}} - \frac{1}{\lambda_{\text{Ra}}} \right] \text{ cm.}^{-1}$			
Ethylbenzene ^a	Diphenyl ether ^b	Diphenylmethane	Methane ^c (liq.)
153	231	178 (broad)	
482	309	468 (He)	
547		520	
620	615	599	
768	748	722	
962	794	791	
1003	1005	971	
1029	1021		
1157	1153		
		1170	
1203	1195		
1384			
1440		1425	
1604	1590		
		1659 (broad)	
2933		2898	2909
			2953
2962			2999
3002			3023
3052		3038 (broad)	3047
3063	3062		3071

^a Kohlrausch, "Der Smekal-Raman Effekt," 1931, p. 329, $[\Delta\bar{\nu}]$ = mean value.

^b Kohlrausch, *ibid.*, p. 332.

^c McLennan, Smith and Wilhelm, *Trans. Roy. Soc. Canada*, 23, 279 (1930).

under ordinary conditions became yellow when exposed to the light of the mercury arc. This color disappeared when the substance was distilled *in vacuo*, but returned again upon exposure to the mercury light.

Results for normal butyl and normal hexyl bromides are recorded in Tables II and III. Plate I shows the rapid decomposition of the bromide under strong illumination both with and without the quinine sulfate filter. By cooling the Raman tube with water passed through a copper coil, a photograph of butyl bromide was obtained which showed a comparatively weak background and, therefore, could be used for measuring the Raman lines excited by both the 4046 and the 4358 mercury groups. A comparison of these lines with the ones given by Kohlrausch⁸ is found in Table II. Hexyl bromide, illuminated with the use of a filter, gave the lines recorded in Table III. In Tables IV and V are listed the wave lengths and wave numbers for the Raman lines of normal amyl, normal hexyl, and normal heptyl mercaptans together with the frequencies of the Raman lines of isoamyl and normal butyl mercaptans studied by Venkateswaran.⁹

TABLE II
RAMAN LINES OF NORMAL BUTYL BROMIDE

λ_{Ra} Å.	Exc. Hg line λ_{Ra} Å. $\Delta\nu_{Ra}$	4046 $\Delta\nu_{Ra}$	$\Delta\nu_{Ra}$ (K) ^a
4407.5-4411.2	254- 274	271- 291	279 (2)
4431.5	377	394	
4442.0-4447.5	431- 458	448- 475	
4462.3-4468.5	533- 564	550- 581	557 (5)
4479.5-4483.5	619- 639	636- 656	637 (2)
4503	736	753	
			794 (1/2)
4512	780	797	
			853 (1/2)
4524.5	841	858	
			1057 (1/2)
4598.3	1196	1213	1139 (1)
4669 -4674	1526-1548	1543-1565	1257 (1b)
			1440 (2b)
4969.5-4997.5	2819-2933	2836-2950	
			2865 (5)
			2930 (3)
			2962 (4)

^a (K) = Kohlrausch, "Der Smekal-Raman Effekt," p. 308.

Discussion

Studies of Petrikaln and Hochberg¹⁰ show no Raman lines but continuous spectra for solutions of diphenylmethane in alcohol and triphenylmethane

⁸ Kohlrausch, "Der Smekal-Raman Effekt," 1931, p. 329.

⁹ Venkateswaran, *Indian J. Physics*, **5**, 219 (1930).

¹⁰ Petrikaln and Hochberg, *Z. physik. Chem.*, **B3**, 217 (1929).

TABLE III

RAMAN LINES OF NORMAL
HEXYL BROMIDE

Exciting line = Hg 4358.6

w = weak s = strong

λ_{Ra} Å.	$\Delta\nu$
4387	149 (w)
4409.8	267 (w)
4432	380 (w)
4458	512 (s)
4468.5-4471.8	564-581 (s)
4480.5	626 (w)
4484.8-4489.2	644-668 (s)
4492	682 (w)
4497.5	708 (w)
4503.7	739 (w)
4508.6	764 (w)
4521.5	826 (w)
4529 -4536.7	864-901 (s)
4552	977 (s)
4572.6-4583.5	1074-1126 (s)
4593.5	1173 (w)
4603	1219 (w)
4613	1266 (s)
4623.8	1316 (s)
4630	1345 (w)
4640	1396 (w)
4650.3-4658	1439-1475 (s)
4927	2647 (w)
4937.5	2690 (w)
4877.5-5010.5	2853-2985 (s)
5021	3027 (s)

TABLE IV

RAMAN LINES OF MERCAPTANS

[λ in Ångström Units]

n-Amyl	n-Hexyl	n-Heptyl
4387.6		4409
4424.8	4425.7	4430.5
4456	4457.5	4445.8
4474	4479	4461.5
4484 -4488.5	4485.6-4491.5	4469.6
4496	4497.3	4478.8
4508.3	4505.2	4487.5-4491.7
4520	4517.7	4498.8
4532.6	4521.2	4507
4537.8	4534.6	4517.4
4556.8	4539	4525
4566.8	4553.5	4537
4572.3	4576.3	4576.3
4580.2	4584.3	4585.6
4598.2	4592	4594.3
4606.5	4600.3	4600.3
4612	4613.2	4614.5
		4620.7
4621.7	4624	4624.8
4628.6	4635.4-4643.4	4628
4643		
4648.6-4654.5	4650.2-4658.4	4634
4665.6	4672.8	4646
4896	4903.2	4651.2-4662.3
4908.5	4910.8	4901
4926		
4936.5	4927.5	4910.6
4952	4957.5	4944.5
4970.5	4974.5	4955
4977 -4989	4979 -5002.5	4978 -5014.5
5011.5-5015.5	5010.7	
5024	5019.5	5025

in ether. However, in the present case, when diphenylmethane was illuminated by the helium line, λ 3888.6, a continuous background did not accompany the Raman spectrum.

Calculated frequencies for the stretching and bending of non-polar chemical bonds have been identified with known Raman lines.¹¹ A comparison of the Raman lines for diphenylmethane with those for diphenyl-ether, ethylbenzene, and methane, obtained by other investigators, shows definitely that certain frequencies can be attributed to vibrations of particular molecular groups and linkages. The lowest frequency, 178 cm^{-1} which does not appear in methane, has a corresponding value in ethylbenzene and diphenyl ether. This frequency is attributed to the bending of the

¹¹ Andrews, *Phys. Rev.*, **36**, 544 (1930).

TABLE V
RAMAN LINES OF MERCAPTANS

$$[\Delta\nu] = \left[\frac{1}{\lambda_{\text{ex.}}} - \frac{1}{\lambda_{\text{Ra}}} \right] \text{cm.}^{-1}$$

b = broad. V = Venkateswaran, *Ind. J. of Phys.*, 5, 219 (1930).

n-Amyl	Isoamyl ^V	n-Hexyl	n-Butyl ^V	n-Heptyl
152	279 (5b)	348	298 (1)	262
343	422 (3b)		333 (2)	372
{ 502 }		{ 509 }	437 (0)	450
{ 592 }		{ 617 }	656 (6)	{ 529 }
{ 642-664 }	659 (5)	{ 650-679 }	707 (0b)	{ 570 }
701	719 (2)	708		{ 616 }
761	741 (2)	747	843 (0)	{ 659-680 }
819	818 (1b)	818		715
881	855 (0)	825	889 (0b)	755
906	929 (0)	891	951 (1)	807
998	955 (1)	912		
1046	1038 (0b)	982	1049 (1b)	844
1072	1114 (0b)	1091	1106 (0)	902
1110		1130		1091
1196	1185 (0b)	1166		1136
1235	1287 (1)	1205	1296 (2b)	
		1266		1177
1261	1300 (1)			1205
		1317		
1306	1337 (2)		1361 (0b)	1282
1338		{ 1370-1407 }		1300
{ 1405 }	1470 (6)	{ 1439-1477 }		1321
{ 1431-1459 }		1543	1438 (3b)	1336
1510		2548		1364
2519				1420
2570	2574 (10)	2580	2574 (10)	
2643		2649		{ 1443-1494 }
				2539
2686		2772		2579
2749				2718
2824		2841		2762
2851-2899	2870 (10b)	2859-2945	2869 (8b)	
2989-3005	2929 (7b)	2986	2905 (7b)	2855-3001
3039	2962 (10b)	3021	2934 (10b)	3042

C-C-C linkage. Vibrational frequencies in the 900-1200 cm.^{-1} region are associated with the stretching of the C-C bond, and occur in every case except methane. The calculated value for the H-C-H bending motion is 1430 cm.^{-1} . Ethylbenzene and diphenylmethane show Raman lines with frequencies of 1440 cm.^{-1} and 1425 cm.^{-1} , respectively, whereas diphenyl ether shows no frequency in this region. The frequency 2898 cm.^{-1} and the broad band at 3038 cm.^{-1} indicate the difference between the C-H vibration of the aliphatic and aromatic linkages, both of which are present in diphenylmethane.

Differences in the values of corresponding Raman lines of butyl bromide, calculated from the two exciting mercury lines, Table II, are likely due to discrepancy in determining the true micrometer readings for the centers of the exciting mercury lines. The breadth and increased intensity of these lines toward the long wave length side make true readings difficult. This explanation is supported by the fact that practically the same variation occurs for each respective wave number. The wave numbers calculated from the 4046 mercury line agree more closely with the average values listed by Kohlrausch.¹² Greater accuracy is attained in measuring these lines since they fall in the shorter wave length region of higher dispersion than the Raman lines from the 4358 mercury line. Frequencies 1057 cm^{-1} and 1139 cm^{-1} recorded by other investigators for butyl bromide¹² were not found; however, hexyl bromide gave a broad line at 1074–1126 cm^{-1} and a less intense line at 1173 cm^{-1} .

Mercaptans higher in the series than butyl mercaptan give at least twenty Raman lines. There seems to be only a slight increase in the number of lines after the molecule has added the fifth carbon atom to its chain. In Table V each group of values in brackets represents but one characteristic Raman frequency, as all values except the last in each group can be attributed to the 4339 and 4348 mercury lines found in the exciting mercury group. Raman and Krishnan¹³ give 15, 30, and 200 as the relative intensities of the mercury lines λ 4339, λ 4347, and λ 4358. Therefore, duplication of weak- and high-frequency Raman lines by the two weak mercury lines seems improbable. Raman frequencies in the 2600 cm^{-1} region may be false, since there is a strong mercury line, λ 4916, in this region. The lines in the neighborhood of 2900–3000 cm^{-1} are very diffuse, and in the case of heptyl mercaptan completely overlap each other.

Several interesting relations from the data are noted. The close agreement in corresponding Raman lines for the mercaptans fails in the lower frequency region where the Raman frequencies characteristic of the wave motion of the molecule as a whole depend upon the length and modification of the carbon chain.¹¹ The C–S linkage has a strong characteristic frequency at approximately 600 cm^{-1} and two weaker vibrations in the 700 cm^{-1} region. The C–S linkage in thiophene, mercaptans, and alkyl sulfides shows practically the same characteristic oscillations, namely, 607 cm^{-1} and 754 cm^{-1} for thiophene,¹⁴ 659 cm^{-1} and 739 cm^{-1} for mercaptans,¹⁵ and 651 cm^{-1} and 746 cm^{-1} for alkyl sulfides.¹⁶ The single lines in both the 700 cm^{-1} and 300 cm^{-1} regions are replaced in the

¹² Kohlrausch, "Der Smekal-Raman Effekt," 1931, p. 308.

¹³ Raman and Krishnan, *Indian J. Physics*, **2**, 399 (1928).

¹⁴ Venkateswaran, *Indian J. Physics*, **5**, 145 (1930).

¹⁵ Venkateswaran, *ibid.*, p. 219.

¹⁶ Venkateswaran, *ibid.*, **6**, 51 (1931).

higher members of the mercaptans by two lines in each region. The S-H linkage at approximately 2575 cm.^{-1} is identical with the S-H frequency of 2575 cm.^{-1} for hydrogen sulfide.¹⁷ This indicates that the frequency of vibration between these two atoms is negligibly affected by other atoms in the molecule. The lower frequency of the S-H linkage at 2575 cm.^{-1} compared with the frequencies of the C-H and O-H linkages at 2930 cm.^{-1} and 3388 cm.^{-1} , respectively, suggests a weaker binding force and more polar nature for S-H than for either C-H or O-H, and agrees with the fact that hydrogen sulfide and the mercaptans show acid properties not exhibited by water and the corresponding alcohols.

Summary

The Raman spectra of diphenylmethane, normal butyl and normal hexyl bromides, and normal amyl, normal hexyl and normal heptyl mercaptans have been photographed and the corresponding lines measured. From a comparison of these lines with those of similar compounds several important relations have been noted.

Lines in the Raman spectrum of diphenylmethane exhibit frequencies characteristic of both aliphatic and aromatic linkages.

The number of Raman frequencies in the case of higher member mercaptans increases with the length of the carbon chain.

The respective values for the C-S and S-H vibrations are almost identical in thiophenes, mercaptans and the alkyl sulfides.

The S-H frequency at 2575 cm.^{-1} , lower than the corresponding C-H and O-H frequencies, indicates a fairly weak binding force and explains the slightly polar properties of hydrogen sulfide and the mercaptans.

¹⁷ Bhagavantam, *Nature*, **126**, 502 (1930).

II. THE RELATIVE INTENSITIES OF CHARACTERISTIC LINES IN RAMAN SPECTRA OF BENZENE-TOLUENE MIXTURES

Introduction

Shortly after the discovery of the Raman effect, Daure¹ pointed out that the Raman spectrum of a mixture of benzene and toluene was the superposition of the spectra of the individual components. Dadiou and Kohlrausch² studied the Raman spectra of fifteen binary liquids and found no change in the characteristic frequencies of the components, except in a few cases where a slight shift occurred in a Raman line associated with a group having a high dipole moment.

Since the intensities of Raman lines produced under a given set of conditions depend upon the molecular density, it seemed probable that Raman spectra should prove useful not only for indicating the quality, but also for estimating the quantity, of substances present in mixtures. As previously noted³ the Raman spectra of benzene-toluene mixtures of varying concentrations were photographed, the intensities of the lines recorded, and the relative heights of the intensity curves compared with the corresponding concentrations of the components taken. Benzene and toluene were chosen for this investigation, primarily because these substances furnish excellent Raman lines for intensity study; also, because they belong to a class of compounds commonly occurring in fractions of light oil mixtures.

In photographing Raman spectra for intensity measurements several factors which condition the density of spectral lines were considered. Experiments of Read and Johnson⁴ show that the blackening produced on a photographic plate is a function of the intensity of light producing the blackening, the time of exposure, the wave length of light, the kind and age of the plate, and the conditions under which the plate is developed. Obviously, optimum results for the comparison study of Raman lines necessitated control of these variables. A method was adopted, therefore, by which as many conditions as possible could be maintained constant.

Apparatus.—The mercury arc was a Hanovia Advanced Research Model. This type, encased with a cooling coil and aluminum reflector and connected with a variable resistance, produced a steady light source

¹ Daure, *Compt. rend.*, **186**, 1833 (1928).

² Dadiou and Kohlrausch, *Physik. Z.*, **31**, 514 (1930).

³ Crigler, *Phys. Rev.*, **38**, 1387 (1931).

⁴ Read and Johnson, *Phil. Mag.*, **11**, 1152 (1931).

for intensity work. The Raman tube was the same as used in Part I. Both the arc and Raman tube were cooled by a small electric fan. A Bausch and Lomb glass prism spectroscope analyzed the scattered light.

A Moll densitometer was used for recording the intensity of the Raman lines. The lines of each spectrum were focused on the face of the thermocouple tube and, as they passed between the light source and the slit of the tube, the intensity of the light falling on the thermocouple varied with the density of the intervening lines. The thermocouple was connected to a galvanometer, and every time a Raman line intercepted the light falling on the thermocouple the mirror of the galvanometer was deflected. This deflection was recorded by a narrow beam of light reflected from the mirror to photographic paper which was mounted on a revolving drum. The drum, in gear with the holder carrying the Raman plate, was run by an electric motor.

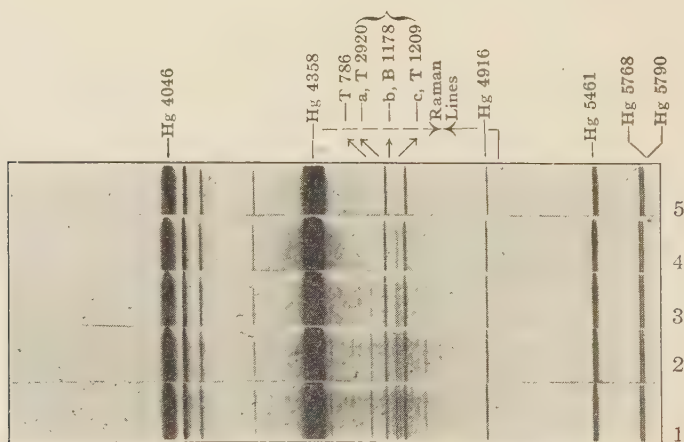


Plate I.—% Benzene-toluene: 1, B 0, T 100; 2, B 25, T 75; 3, B 50, T 50; 4, B 75, T 25; 5, B 100, T 0.

Materials.—Freshly distilled samples of Baker's c. p. benzene, specific gravity 0.88, and Baker's c. p. toluene, specific gravity 0.87, were used in making all mixtures.

The same kinds of photographic materials were used for this work as were used in Part I. Eastman's P. M. C. bromide paper, No. 2, smooth, was used in the densitometer for photographing the intensity curves.

Technique.—Adjustment and collimation of the spectroscope were first secured. After the metal pieces forming the slit were carefully polished, and placed parallel to ensure spectral lines of uniform width, the spectroscope was leveled and the collimator and camera adjusted so that when the

mercury arc was placed in front of the spectroscope a horizontal spectrum of mercury lines was projected on the ground glass plate of the camera. The Raman tube, firmly supported by an iron clamp, was brought in line with the collimator by focusing an image of the tube in the center of the spectroscopic field. The light from the mercury arc was reflected back and forth through the liquid by a tin-foil reflector. The face of the Raman tube was almost tangent to the end of the spectroscope. This arrangement prevented stray light from entering the slit. The proximity of the tube to the spectroscope increased the intensity of the incident light.

After alignment of the apparatus, all parts except the Raman tube were left intact for each series of photographs made. In changing the material in the tube it was found more convenient to leave the tube clamped to the ring stand and to move the stand and Raman tube as a unit. In this way, each time the tube was emptied and refilled, it could readily be placed in the original position by adjusting the position of the stand. Shadows of the Raman tube formed on the box of the mercury arc and reflections from the uneven edges of the Raman tube face served as excellent reference marks for adjusting and replacing the tube.

The voltage across the mercury arc was regulated by a rheostat in series with the arc, and did not vary more than one or two volts during any exposure.

After the apparatus was in line with the spectroscope and the voltage across the arc carefully regulated, the width of the slit and time of exposure were varied alternately until a combination of the two yielded spectra showing marked and measurable variations with small changes in concentration. With two-hour exposures the best results were procured when the mercury arc was maintained at 50 volts, the temperature of the Raman tube was kept at 35°, and the width of the slit was 0.07 mm.

All plates were developed under the same conditions. The solutions used in developing and in fixing the image and the water used for washing the plates were kept at 0° by immersing the developing trays in an ice-bath. Each plate was developed for ten minutes in 100 cc. of Rhodinal solution, 1 to 20 dilution, then rinsed in ice

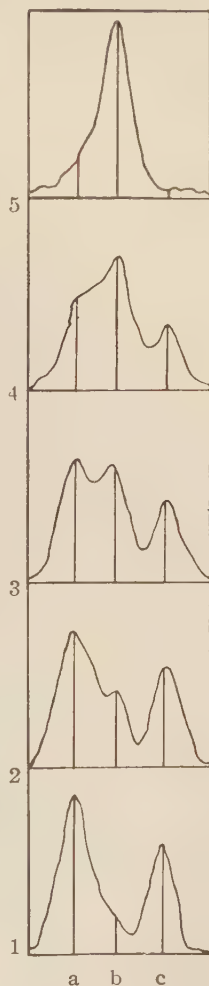


Fig. 1.—Section of photometric curve.
% Benzene-toluene:
1, B 0, T 100; 2, B 25, T 75; 3, B 50, T 50; 4, B 75, T 25; 5, B 100, T 0.
 $\Delta\nu$ Raman line: a, T 2920 [Hg 4046]; b, B 1178 [Hg 4358]; c, T 1209 [Hg 4358].

water and fixed in a solution of Eastman's hypo for ten minutes. Care was taken to wash the plate free from the salt left by the hypo solution.

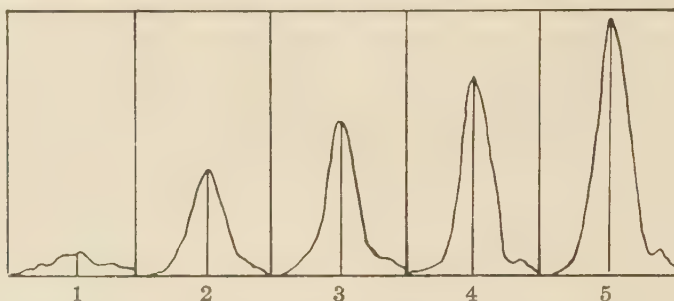


Fig. 2.—Intensity curve of toluene line $\Delta\nu$ 786. % Benzene-toluene: 1, B 100, T 0; 2, B 75, T 25; 3, B 50, T 50; 4, B 25, T 75; 5, B 0, T 100.

The trays in which the plate was developed were agitated to keep the solution constantly washing the gelatin surface in order to leave an even film on the glass. Plates treated in this manner and carefully dried showed a uniform, fine-grained background, with well-developed lines suitable for photometric measurements.

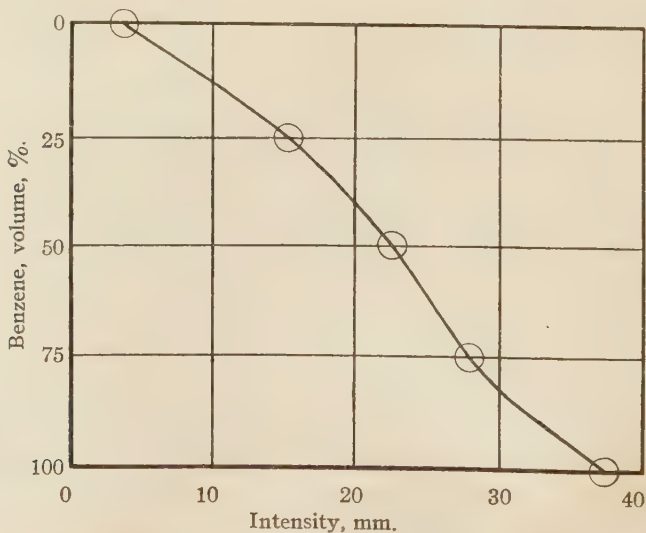


Fig. 3.—Relative intensity of characteristic benzene line [$\Delta\nu = 1158$] with change in concentration.

In measuring the relative heights of the Raman lines the same horizontal section of each spectrum was chosen for each series of photographs in order that any gradation or imperfection in one spectrum, due to experimental conditions, would be recorded for every spectrum.

Halation around the stronger mercury lines and a slight continuous background prevented the use of a single standard line for measuring all of the Raman lines. Instead, a line for each group of Raman lines was chosen, and this same line used as reference throughout a series of measurements.

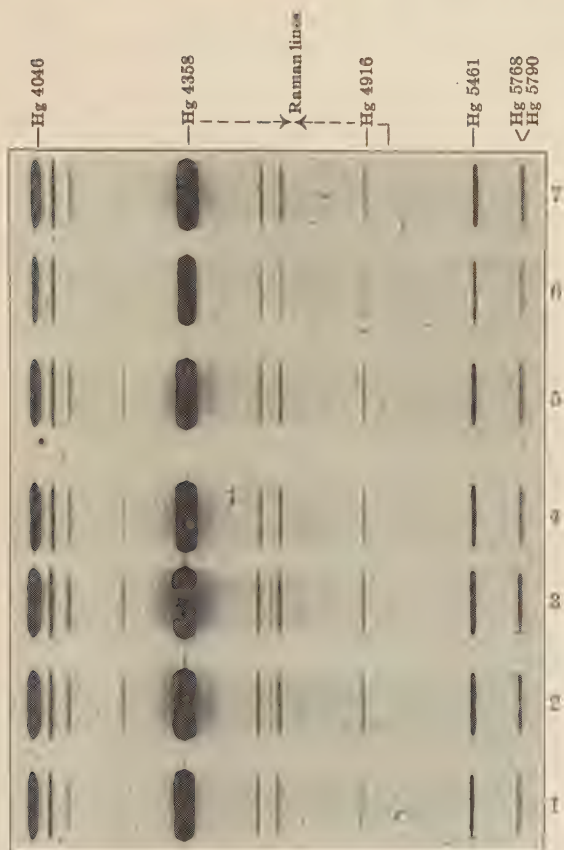


Plate II.—Variation of slit and exposure: 1, [-2]—1 hr.; 2, [-2]—2 hrs.; 3, [-4]—2 hrs.; 4, [-4]—1 hr.; 5, [+2]—2 hrs.; 6, [+2]—1 hr.; 7, [-7]—1 hr.

Good intensity measurements seemed to depend largely upon the nature of the photographs and the technique of using the densitometer. After spectra of sharp contrast and uniform background were obtained it was necessary, due to the sensitivity of the densitometer, to duplicate the photometric curves before making final intensity measurements. Raman photographs were duplicated which gave photometric curves in which the height of the most intense lines varied less than 1 mm. Likewise,

duplicate intensity curves of the same photograph showed less than a 0.5 mm. change for any Raman line.

Results

Photographs of the first Raman spectra of mixtures of 25% variation in concentration are reproduced in Plate I where the appearance, disappearance, and the change in density of certain Raman lines can be observed. Further evidence of these intensity changes is shown by the photometric curves in Figs. 1 and 2 and by the intensity curves plotted in Fig. 3.

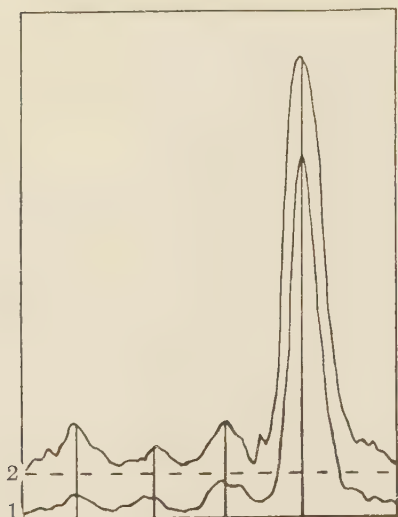


Fig. 4.—Change of curve with length of exposure: 1, exposure, 1 hour; 2, exposure, 2 hours.

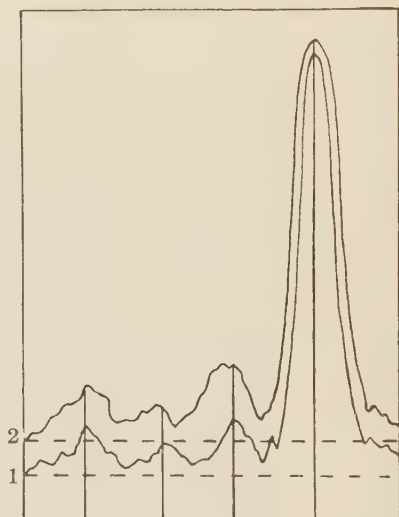


Fig. 5.—Change of curve with width of slit: 1, slit, 0.071 mm.; 2, slit, 0.089 mm.

At first, all of the Raman lines on the long wave length side of the 4358 mercury line were measured, but it was soon discovered that the group of Raman lines in the region between 600 and 1000 cm^{-1} exhibited the greatest variations in intensity with change in concentration. The work, therefore, was devoted to measuring and comparing lines falling within this particular region.

The fact that the first results did not show measurable differences for small changes in concentration suggested improvement in technique. The importance of finding a favorable combination of slit and exposure, in photographing Raman spectra for intensity study, is strikingly brought out in the gradations shown in the spectra of Plate II and in the photometric curves of Figs. 4 and 5. From these illustrations it is evident that a narrow slit with long exposure is preferable to a wide slit with short

exposure. Spectrum (5) in Plate II proved the most satisfactory type for the present work.

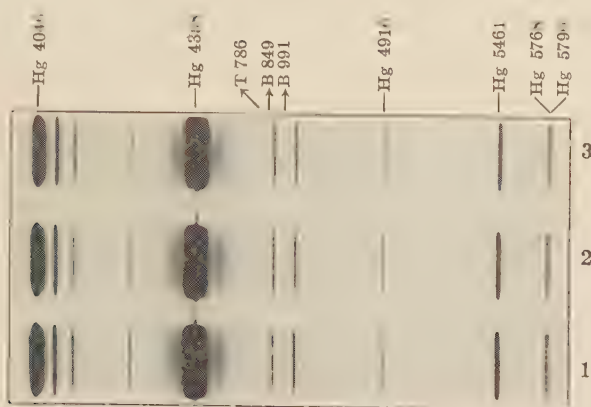


Plate III.—% Benzene-toluene: 1, B 95, T 5; 2, B 90, T 10; 3, B 85, T 15.

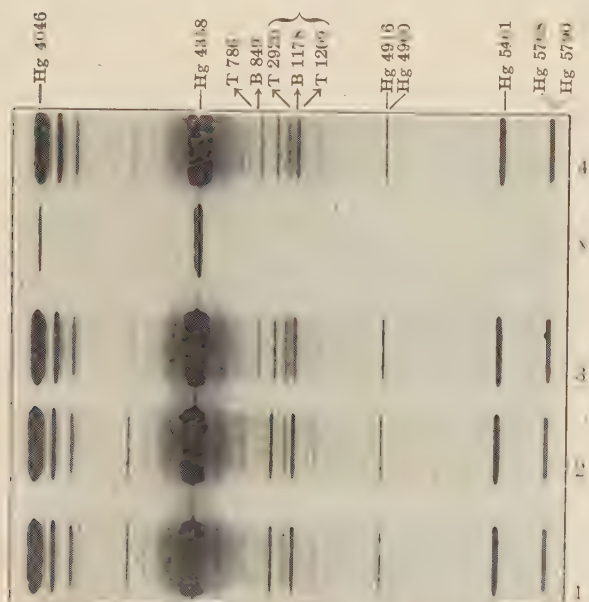


Plate IV.—% Benzene-toluene: 1, B 95, T 5; 2, B 95 T 5; 3, B 0, T 100; 4, B 5, T 95; x, Hg lines.

Plates III and IV, Figs. 6 and 7, and Tables II, III and IV give results obtained under the optimum conditions and show that 5% changes in concentration are easily measurable.

TABLE I

RELATIVE INTENSITY OF RAMAN LINES FOR 25% CHANGE IN CONCENTRATION OF BENZENE-TOLUENE

Exciting mercury line		4358		4046		4358		4358
Raman line		T 786		T 2920		B 1178		T 1209
% (vol.) B-T	Mole, % B-T		ΔI		ΔI		ΔI	ΔI
100-0	100-0	2.7		8.5		37.2		1.5
			17.2		10.2		9.0	11.7
75-25	78-22	19.9		18.7		28.2		13.2
			7.1		6.9		5.6	2.1
50-50	54-46	27.0		25.6		22.6		15.3
			8.2		2.2		7.5	3.7
25-75	28-72	35.2		27.8		15.1		19.0
			10.5		4.4		11.4	3.6
0-100	0-100	45.7		32.2		3.7		22.6

TABLE II

RELATIVE INTENSITY OF RAMAN LINES [Ht. in mm.]

Exciting mercury line	4358	4358	4347	4358
Raman line	T 786	B 849	B 991	B 991
% (vol.) B-T	ΔI	ΔI	ΔI	ΔI
95-5	6.3	10.1	13.0	92.7
	1.5	1.1	2.0	1.6
90-10	7.8	9.0	11.0	91.1
	1.2	1.2	1.0	0.5
85-15	9.0	7.8	10.0	90.6

TABLE III

DIFFERENCES IN HEIGHT BETWEEN B 991 [4358 Hg] AND NEIGHBORING LINES [Ht. in mm.]

Exciting mercury line	4358	4358	4347
Raman line	T 786	B 849	B 991
% (vol.) B-T	ΔI	ΔI	ΔI
95-5	85.2	81.7	78.5
	2.9	0.3	0.7
90-10	82.3	82.0	79.2
	2.0	0.3	0.7
85-15	80.3	82.3	80.5

TABLE IV

RELATIVE INTENSITY OF RAMAN LINES [Ht. in mm.]

Exciting mercury line	4358	4358	4046	4358	4358
Raman line	T 786	B 849	T 2920	B 1178	T 1209
% (vol.) B-T	ΔI	ΔI	ΔI	ΔI	ΔI
0-100	31.2	54.0	39.0	11.7	23.2
	3.7	3.5	3.7	4.8	0.7
5-95	27.5	50.5	35.3	16.5	27.5

Discussion

As can be seen in the spectra photographed, the complete mercury spectrum was used in producing Raman lines for intensity measurements. In the section chosen for study the Raman lines were excited by the mercury lines $\lambda 4046$, $\lambda 4339$, $\lambda 4347$ and $\lambda 4358$. There was an advantage in using the high frequency Raman lines excited by the 4046 mercury line, as they were more intense than the corresponding lines excited by the 4358 mercury line. In the case of high frequency Raman lines the intensity increases with the frequency of the exciting line much more rapidly than the fourth power law.⁵

A study of Raman spectra and of intensity values shows that the Raman line at 786 cm.^{-1} is by far the best indicator for toluene. This characteristic toluene line was perceptible in the spectrum of a mixture containing 5% toluene obtained after only one hour of exposure. However, short exposures necessitating a fairly wide slit are not suitable for intensity comparisons.

The concentration of benzene in a mixture can be estimated from the intensity of either the 849 cm.^{-1} frequency or the 991 cm.^{-1} frequency, both strong Raman lines of benzene. It is interesting to note that the weak 4347 mercury line excites a Raman line at 991 cm.^{-1} which apparently gives with the densitometer greater intensity variation with small changes in concentration than the same line excited by the strong 4358 mercury line.

In the case of benzene-toluene mixtures the toluene line at 1002 cm.^{-1} might be expected to interfere somewhat with the actual height and contour of the benzene line at 991 cm.^{-1} . Although the shape of the curve for this line is slightly changed and the peak of the curve shifted with increase in toluene, it invariably decreases in height with decrease in the concentration of benzene.

Table III shows a method for measuring the intensities in terms of the differences in height between a given Raman line, chosen as standard,

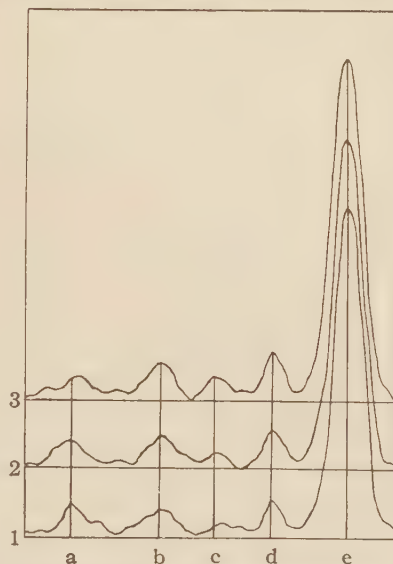


Fig. 6.—Section of photometric curve. % Benzene-toluene: 1, B 85, T 15; 2, B 90, T 10; 3, B 95, T 5. $\Delta\nu$ Raman line: a, T 786 [Hg 4358]; b, B 849 [Hg 4358]; c, B 991 [Hg 4339]; d, B 991 [Hg 4347]; e, B 991 [Hg 4358].

⁵ Sirkar, *Indian J. Physics*, 5, 593 (1930).

and each neighboring Raman line. Perhaps this method is less subject to error than the more direct method of measuring relative heights, because in using the differences between the peaks of lines the arbitrary choice of a reference line is eliminated. Since measurements of this kind show a difference of 50 mm. from the top of a strong toluene line in 100% toluene to the top of a strong benzene line in 100% benzene, surely much less than 5% change in concentration should be detectable from intensity measurements.

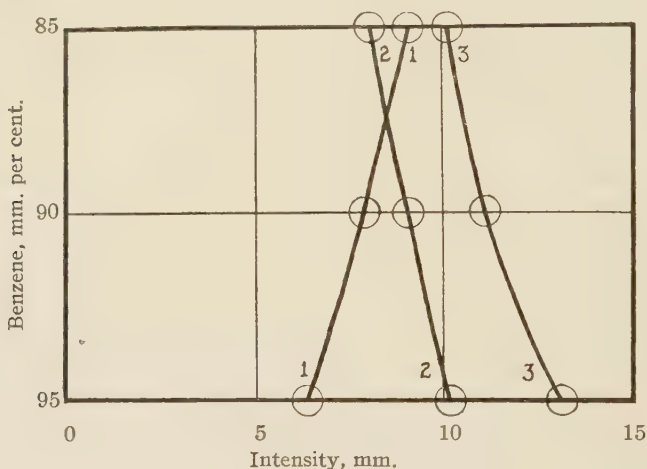


Fig. 7.—Relative intensity of Raman lines in benzene-toluene mixtures: 1, T 786; 2, B 849; 3, B 991.

The relative intensities of Raman lines, which depend upon molecular density,⁶ intensity and frequency of the exciting line,⁵ and experimental conditions under which the lines are produced,⁷ offer excellent opportunity and possibility for investigating the nature and determining the composition of mixtures and solutions. Recently the sensitivity of Raman lines in testing for the presence of the double bond has been reported to be as high as 1.2–2.4%.⁸

Summary

By means of a simple experimental procedure, measurements of the relative intensities of characteristic Raman lines of benzene-toluene mixtures were obtained which show with 5% change in the concentration of either benzene or toluene a change of several millimeters in the height of the photometric curve.

⁶ Cabannes and Daure, *Compt. rend.*, **186**, 1533 (1928).

⁷ Merton and Nicholson, *Phil. Trans.*, **A217**, 237 (1918); Read and Johnson, *Phil. Mag.*, **11**, 1152 (1931).

⁸ Lespieau, Bourquel and Wakeman, *Compt. rend.*, **193**, 238 (1931).

BIOGRAPHY

Elizabeth Aylor Crigler was born in Lutherville, Maryland, August 23, 1905. She moved with her parents to Charlotte, North Carolina in 1915, and completed her elementary and secondary education in the public schools of that city. In 1927 she was graduated from Goucher College with a Bachelor of Arts degree. During the years 1927-1930 she was enrolled in the School of Higher Studies of The Johns Hopkins University. The summer quarter of 1928 was spent at The University of Chicago. Since 1930 she has been instructor in chemistry at MacMurray College, Jacksonville, Illinois.

